III.B.11 Desulfurization of High-Sulfur Jet Fuels by Adsorption and Ultrasound-Assisted Sorbent Regeneration

Objectives

- Develop easily regenerated, stable and high sulfur capacity sorbent for desulfurization of jet fuels containing high sulfur concentrations.
- Develop a solvent regeneration technique assisted by ultrasound in addition to thermal regeneration.

Accomplishments

- Developed a stable and high sulfur capacity sorbent of $PdCl_2$/AC (palladium chloride/activated carbon) that exhibits excellent selective adsorption capability for sulfur-containing compounds from a model jet fuel (400 ppmw-S). More than 20 ml of the model jet fuel was desulfurized to below 1.0 ppmw-S per gram sorbent.
- For the spent $PdCl_2$/AC sorbent, about 65 wt% sulfur can be desorbed in 30 minutes using ultrasound at 50°C. This result indicates that the spent $PdCl_2$/AC sorbent could be effectively regenerated by ultrasound.

Introduction

Liquid-phase sulfur removal from jet fuels is a key area which will help enable the fuel cell program. A new, novel technology of adsorptive desulfurization is explored in this project. In the refineries, desulfurization is accomplished by hydrodesulfurization (HDS), which is a catalytic process using high-pressure hydrogen (40-100 atm) and high temperatures (300-340°C) over a NiMo/alumina catalyst. The adsorptive desulfurization technology being explored involves a simple one-step process under ambient temperature and pressure. If successful, the new technology would replace the conventional technology for desulfurization of petroleum products, and it could also be used for desulfurization as a polishing step for fuel cell applications. At a minimum, new results will be generated from this project that will advance the field of sorbent development for environmental applications.

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Approach

As described below, a number of sorbents were prepared for this work. The sorbents were prepared by standard incipient wetness impregnation and thermal dispersion methods. The selective adsorption experiments using different sorbents were performed in vertical custom-made quartz adsorbers as described elsewhere [1-3]. The fuels collected during the experiments were analyzed using a gas chromatograph equipped with a flame photometric detector. The spent $PdCl_2$/AC sorbent was regenerated by desorption of sulfur compounds in a solvent with heating and ultrasound technique.

Results

After *in situ* activation of the adsorbent, the fuel was allowed to contact the bed, and the sulfur contents in the effluent samples were monitored periodically. Breakthrough adsorption curves were generated by plotting the transient sulfur concentration normalized by the feed versus cumulative fuel volume normalized by total bed weight. The sulfur adsorption amounts (normalized by adsorbent weight) were obtained after integration of the area above the breakthrough curves.

Figure 1 shows the breakthrough adsorption of total sulfur during desulfurization of a model jet fuel with the $PdCl_2/Al_2O_3$, CuCl/AC and $PdCl_2$/AC adsorbents. The model jet fuel was prepared to simulate the commercial jet fuels, and it contained 150 ppmw-S benzothiophene (BT), 250 ppmw-S methyl benzothiophene (MBT) and 700 ppmw naphthalene, in 19.75 wt% benzene + 80 wt% n-octane. It is clear that all of the sorbents are capable of removing benzothiophene and 2-methylbenzothiophene. For the same feed, $PdCl_2$/AC showed the highest capacities among the adsorbents studied. The breakthrough and saturation capacities for total sulfur were 0.126 and 0.187 mmol/g respectively, indicating strong interactions with benzothiophene and 2-methylbenzothiophene molecules. It was found that more than 20 ml of the model jet fuel was desulfurized to below 1.0 ppmw-S per gram sorbent on the fresh $PdCl_2$/AC. From the breakthrough curves, it was also found that the $PdCl_2$/AC sorbent has higher

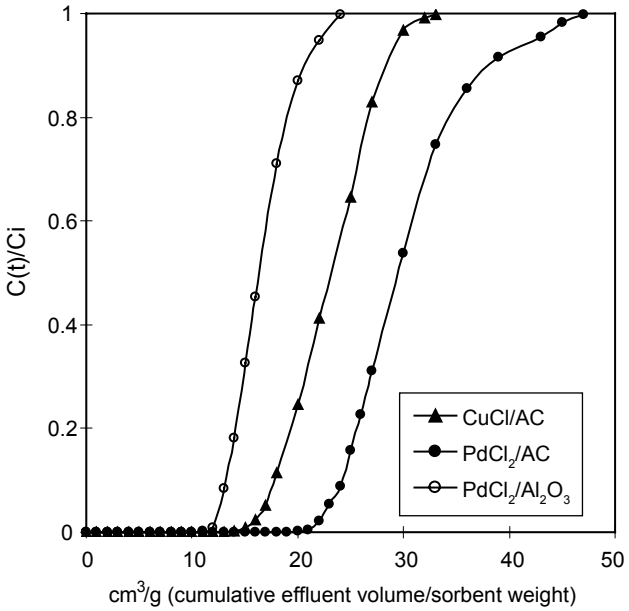

FIGURE 1. Breakthrough of total sulfur in a fixed-bed adsorber with fresh $PdCl_2/Al_2O_3$ (○), CuCl/AC (▲) and $PdCl_2$/AC (●), for model jet fuel (150 ppmw-S BT and 250 ppmw-S MBT in 19.75 wt% benzene + 80 wt% octane containing 700 ppmw naphthalene) at room temperature. Ci is the total sulfur concentration of the feed at flow rate 1 cm^3/10 min (S.V. = 4.6 h^{-1}).

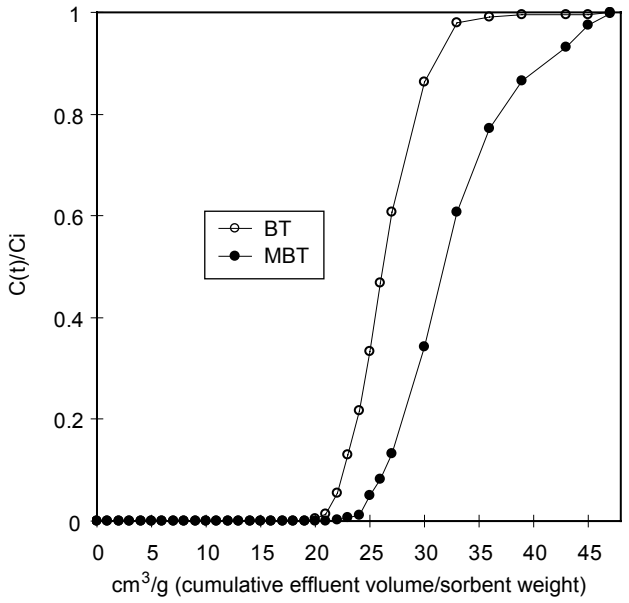

FIGURE 2. Breakthrough of BT and MBT sulfur in a fixed-bed adsorber with fresh $PdCl_2$/AC, for model jet fuel (150 ppmw-S BT and 250 ppmw-S MBT in 19.75 wt% benzene + 80 wt% octane containing 700 ppmw naphthalene) at room temperature. Ci is the total sulfur concentration of the feed at flow rate 1 cm^3/10 min (S.V. = 4.6 h^{-1}).

sulfur capacity than CuCl/AC sorbent has. Since the amount of $PdCl_2$ salt (1.31 mmol·g^{-1}) on activated carbon is similar to the amount of CuCl (1.11 mmol·g^{-1}) on activated carbon, it is reasonable to conclude that the metal salt $PdCl_2$ contributed significantly toward adsorption of the sulfur-containing compounds.

To compare the sulfur capacity of $PdCl_2$ on different supports, desulfurization by $PdCl_2/Al_2O_3$ was tested under the same feed conditions. From the breakthrough curves, the $PdCl_2$/AC sorbent adsorbed almost twice as much sulfur compared with $PdCl_2/Al_2O_3$. This showed that the activated carbon is a more effective support than Al_2O_3 for the $PdCl_2$ supported sorbents for desulfurization of fuel containing benzothiophene and substituted compounds.

From the above results, it is concluded that the metal ion Pd^{2+} is stronger for π-complexation than Cu^+, and the activated carbon is a more effective support than Al_2O_3.

Figure 2 shows the results of desulfurization of model jet fuel over the $PdCl_2$/AC sorbent. The results show that the sorbent can remove 0.069 and 0.091 mmol of benzothiophene sulfur per gram at breakthrough and saturation, respectively, while the sorbent was capable of removing 0.126 and 0.187 mmol of methylbenzothiophene sulfur per gram at breakthrough and saturation for the same model jet fuel, respectively. Figure 2 shows that the $PdCl_2$/AC had a

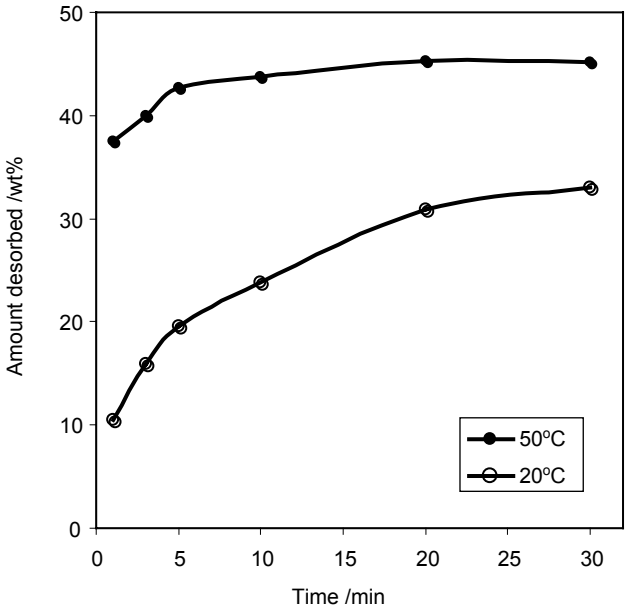

FIGURE 3. Amount of total sulfur desorbed (in percent, g S/g sorbent) from spent $PdCl_2$/AC sorbent regenerated at 20°C (○) and 50°C (●) in a static system with 30 wt% benzene and 70 wt% octane.

selectivity towards heavier, substituted benzothiophene over the nonsubstituted one.

After saturation by the model jet fuel, the spent sorbent was regenerated at 20°C and 50°C in a static bath of solvent. Figure 3 shows the results of desorption

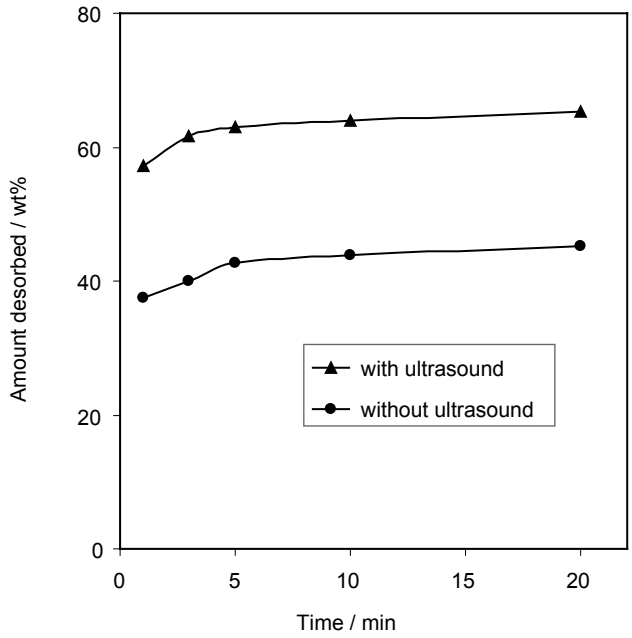

FIGURE 4. Amount of total sulfur desorbed (in percent, g S/g sorbent) from spent $PdCl_2$/AC using ultrasound and no ultrasound at 50°C in a static system with 30 wt% benzene and 70 wt% octane.

in the mixture of 30 wt% benzene and 70 wt% n-octane. The amount of sulfur desorbed depends on the time and temperature. Figure 3 shows that approximately 35 wt% of the total sulfur in the sorbent was desorbed at 20°C and approximately 45 wt% of the total sulfur in the sorbent was desorbed at 50°C after 30 minutes in the solvent.

In our previous study [3], it was found that ultrasound is an effective technique for regenerating spent $CuCl/Al_2O_3$ sorbent. In this work, the ultrasound technique was also applied to regenerate the spent $PdCl_2$/AC sorbent at 50°C. Figure 4 shows the results of desorption with ultrasound and without ultrasound at 50°C. The amount of sulfur desorbed was higher with ultrasound, 65 wt% desorption vs. 45 wt% without ultrasound. This result indicates that the spent $PdCl_2$/AC sorbent could be effectively regenerated by the ultrasound technique.

Conclusions and Future Directions

- $PdCl_2$/AC sorbent showed a high desulfurization capacity for removing sulfur-containing compounds from a model jet fuel. More than 20 ml of the model jet fuel can be desulfurized to below 1.0 ppmw S per gram of sorbent on the fresh $PdCl_2$/AC.
- It was found that the spent $PdCl_2$/AC sorbent could be effectively regenerated by ultrasound. For the spent $PdCl_2$/AC, about 65 wt% of adsorbed sulfur can be desorbed in 30 min using ultrasound at 50°C.

Special Recognitions & Awards/Patents Issued

Two US Patents were issued as a result of previous work that led to this work:

1. U.S. Patent 7,029,574, "Selective adsorbents for purification of hydrocarbons." (April, 2006).

2. U.S. Patent 7,053,256, "Selective adsorbents for purification of hydrocarbons." (May, 2006).

References

1. Yang, R. T.; Hernández-Maldonado, A. J.; Yang, F. H. *Science* 2003, *301*, 79.

2. Hernández-Maldonado, A. J.; Yang, R. T. *J. Am. Chem. Soc.* 2004, *126*, 992.

3. Hernández-Maldonado, A. J.; Qi, G.; Yang, R. T. *Appl. Catal. B.* 2005, *61*, 212.